

The influence of CH bond polarization on the self-association of 2-acylamino-pyrimidines by NH/CH...O/N interactions: XRD, NMR, DFT, and AIM study

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Abstract The single crystal structures of two 2-acylamino-pyrimidines, where alkyl groups in acyl moiety are *iso*-propyl (**1**) and dichloromethyl (**2**), were solved by X-ray diffraction method. The strength of intermolecular hydrogen bonding interactions depends on the C–H bond polarization increased by exchanging two methyl groups by chlorine atoms in the adjacent substituent. The computational methods provide an additional insight into the intermolecular interactions and are utilized in explaining the differences in the observed crystal structures. The experimental and computational data together explain the differences in the formed aggregates and revealed that these simple substitutions cause crucial changes in the intermolecular interactions.

Keywords Weak interaction · Bond polarization · Hydrogen bonding · Crystal structure · DFT calculations

Introduction

The non-covalent interactions are nowadays explored and used in design and preparation of supramolecular

assemblies [1–3]. Among the classic examples of strongly bound dimers are amides, carboxylic acids, and a plethora of heteroaromatics such as 2-aminopyridine and 2-[1H]-pyridone [4]. In general the hydrogen bonding depends on properties of hydrogen bond donors (D) and acceptors (A) such as the acidity and basicity of interacting groups. It has been shown how hydrogen bonding can be used in designing the shape of aggregate [5–7] in solution and in solid state [8]. Generally, non-covalent intermolecular interactions are influenced by steric effects [9–12], electronic repulsion [11, 13], position of the heteroatoms in the ring [14–16], and cooperative effects [17]. The atoms able to compete for hydrogen bonds (basic or acidic centers) are responsible for the conformational flexibility of NH–CO bond in amides [18–20]. This conformational freedom is restricted in 2,6-bis(acylamino)pyridines preventing their dimerization via quadruple hydrogen bonding while the conformational flexibility is maintained in related pyrimidines [10, 18] possessing an additional nitrogen in the ring when compared with pyridine. The same is realized in comparison of the solid-state structure of 2-acetylaminopyridine [9] versus 2-acetylaminopyrimidine [16] (Fig. 1).

Furthermore, intramolecular hydrogen bonding stabilizes some of these molecules [19, 20]. An increased flexibility of the 2-acylamino substituent in pyrimidine is argued to be due to electron lone pair repulsions between N-3 and carbonyl oxygen [16]. This was confirmed by comparison of the heteroassociation of 2,2'-dipyridylamine versus 2-acetylaminopyrimidine which both contain ADA hydrogen bond motifs with DAD counterparts capable for triple hydrogen bonding [12]. The weak (usually below 16 kJ/mol [21, 22]) CH...O [23–25], CH...N [26, 27], or CH... π [28] interactions may also influence the geometry [29] of self-assembled molecules. The nonconventional CH...O hydrogen bonds have been found in pyridine–

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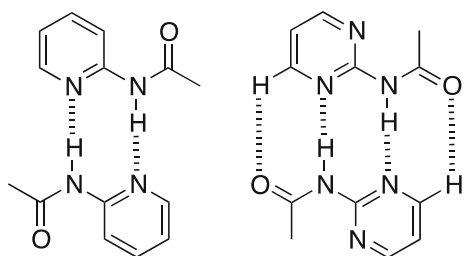


Fig. 1 The solid-state structures of 2-acetylaminopyridine and 2-acetylaminopyrimidine

carboxylic acid co-crystals [30–33], in crystals of *N,N'*-di(2-pyridyl)oxamide [34], and nitromethane entrapped in cyclodextrin [35]. It is commonly known that CH is a weaker hydrogen bond donor than NH/OH due to lower electronegativity of carbon than that of nitrogen and oxygen. During our studies on 2-acylamino-pyrimidines an interesting question arises whether a change in C–H bond polarization would result in formation of intramolecular hydrogen bonding as in some heterocyclic urea derivatives [15, 36–38]. The main goals in the present study are: (a) to check if the intramolecular hydrogen bonding by CH donor is able to limit the conformational flexibility in these molecules, (b) to study how polarization of CH bond by chlorines influences the molecular structure, and (c) to model and interpret the molecular properties via computational methods. It is worth mentioning that in Cambridge Structural Database (CSD) only three similar structures were found revealing that the bifurcation of hydrogen bond in pyrimidine derivatives is not common. These contain aromatic CH...N/O [39, 40] or OH...N/O [41] contacts.

Experimental

The synthesis of **1** and **2** (Fig. 2) was performed as described before [16]. Their dimerization constants were determined by ^1H NMR dilution studies fitted to Benesi-

Hildebrand equation [42]. X-ray diffraction data of **1** and **2** were collected at 123(2) K on a Bruker-Nonius KappaCCD diffractometer with ApexII detector using graphite monochromated Mo- K_α radiation. The details of X-ray crystallography are given in Electronic Supplementary Material (ESM). The solved geometries of **1** and **2** were used as inputs for quantum chemical calculations to validate the intermolecular interactions including the strength of hydrogen bonding. The M05/6-311G(d,p) level of theory, recommended in studying non-covalent interactions [43–46], was applied to monomers and dimers of **1** and **2**. The frequency calculations were run to be sure that the geometry is in energy minima (no negative frequencies were obtained). The transition state for reaction shown in Fig. 3 was optimized with the use of Synchronous Transit-Guided Quasi-Newton algorithm [47, 48]. All optimizations have been run using Gaussian software [49]. The H-BCP properties were calculated with the use of AIM2000 software [50].

Results and discussion

2-Acylamino-pyrimidines either with two methyls (**1**) or chlorines (**2**) in acyl moiety (Fig. 1) gave crystals for X-ray structure determination after slow evaporation of CDCl_3 in NMR tube. Compounds were characterized also by ^1H , ^{13}C , and ^{15}N NMR spectroscopy and by elemental analysis (see ESM).

It has been shown [16] that 2-acetylaminopyrimidine exists in *E* conformation in crystals as dimers stabilized by two NH...N and two CH...O interactions (Fig. 1). The less limited rotation about N7–C8 in pyrimidine is due to an additional nitrogen (N3 differing from pyridine derivatives [9]). In **1** and **2** such a free rotation is not observed and the amide conformation is *Z* in crystal structure as also in 1-adamantyl derivative [16]. The substitution of *i*-Pr group by CHCl_2 results in a different crystal structure although

Fig. 2 The ORTEP [70] plots of **1** and **2** (most hydrogens are omitted for clarity), atom numbering and hydrogen bonding pattern

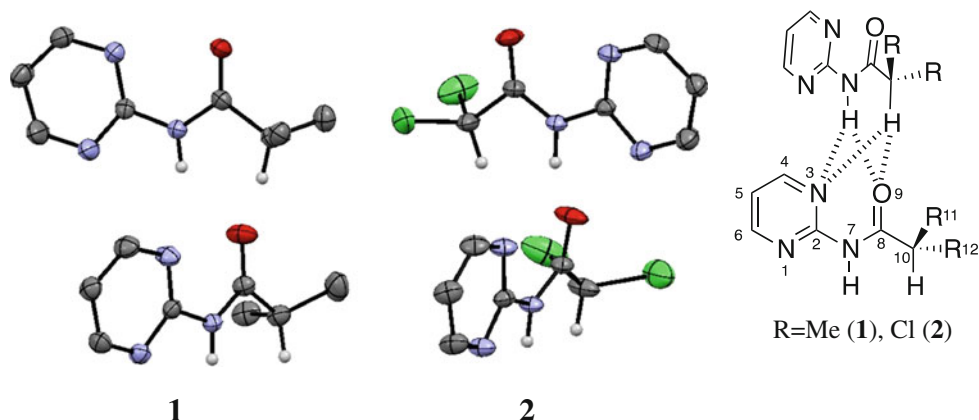


Fig. 3 Open and closed forms of **1** and **2** and the intramolecular hydrogen bonding in the closed form and in a urea derivative

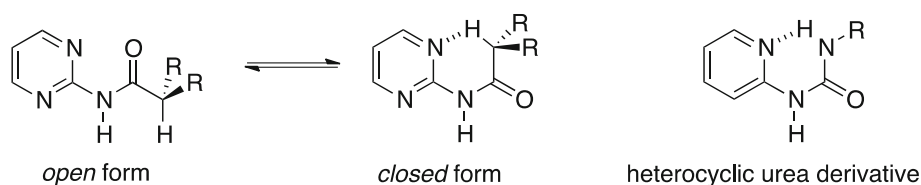


Table 1 Hydrogen bonding geometries in the crystals of **1** and **2**

	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
1				
N(7A)···N(3B) ^a	0.86(5)	2.25(5)	3.073(4)	162(4)
N(7B)···O(9A)	0.91(5)	2.43(5)	3.167(4)	139(4)
N(7B)···N(3A)	0.91(5)	2.26(5)	3.073(5)	148(4)
C(5B)···O(9A) ^b	0.95	2.42	3.287(5)	151
C(10A)···O(9B) ^a	1.00	2.51	3.442(5)	156
C(10B)···O(9A)	1.00	2.49	3.302(5)	138
C(12A)···N(1B) ^c	0.98	2.61	3.496(5)	150
C(11B)···N(1A) ^d	0.98	2.72	3.513(5)	138
C(12B)···N(1A) ^d	0.98	2.70	3.493(5)	139
2				
N(7)···O(9) ^e	0.92(3)	2.18(3)	2.923(2)	137(2)
N(7)···N(3) ^e	0.92(3)	2.38(3)	3.160(3)	143(2)
C(10)···O(9) ^e	1.00	2.48	3.296(3)	139
C(10)···N(3) ^e	1.00	2.61	3.387(3)	134
C(6)···N(1) ^f	0.95	2.70	3.322(3)	123
C(5)···O(9) ^g	0.95	2.71	3.296(3)	120
C(4)···Cl(12) ^g	0.95	2.94	3.747(2)	143

A and B refer to two crystallographically independent molecules in asymmetric unit of **1**

Symmetry transformations to generate the atoms: ^a $x, y, z - 1$; ^b $-x + 2, y + 1/2, -z + 1$; ^c $-x + 2, y - 1/2, -z$; ^d $-x + 1, y - 1/2, -z$; ^e $y + 1/2, -x + 1/2, z - 1/4$; ^f $-y, -x, -z + 3/2$; ^g $y, x - 1, -z + 2$

the methyl groups and chlorine atoms are comparable in size. In structure of **2** molecules are oriented around four-fold axis (Fig. 2; ESM). This is suspected to result from the electronic repulsion of the chlorine atoms. In structure of **1** two molecules are present in asymmetric unit and they show slightly deviating geometry in acylamino group (see ESM). The hydrogen bonding geometries of **1** and **2** are collected in Table 1.

The geometry data show that the substitution of methyls by chlorine atoms causes only clear shortening in N7···O9', C10···N3' intermolecular hydrogen bonding distances (and partly in C10···O9', Table 1). However, out of four intermolecular distances presented in Fig. 2 the hydrogen bond contact N7···N3' is longer in **2** than in **1**. The chains of molecules along the *c*-axis formed by these four hydrogen bonds are connected with adjacent chains by weak C–H···N/O type interactions (also one C–H···Cl in **2**). The distance between ring centroids of adjacent molecules are

Table 2 The properties [density (ρ), Laplacian ($\nabla^2\rho$) of electron density, and hydrogen bond energy (E_{HB} , (kJ/mol))] at H-BCP in **1/2**

H-BCP	ρ	$\nabla^2\rho$	E_{HB}
N7–H7···N3'	0.013/0.012	0.048/0.041	–10.8/–9.6
N7–H7···O9'	0.008/0.015	0.034/0.061	–7.9/–14.1
C10–H···N3'	0.006/0.008	0.017/0.026	–4.1/–6.1
C10–H···O9'	0.009/0.009	0.031/0.032	–7.6/–7.7
Sum			–30.4/–37.5

ca. 5.4 Å in crystals of **1** and 6.1 Å in crystals of **2** (Table S3), which is perfectly understood since the angle between ring planes are 61° and 90°, respectively. While the intermolecular distances clearly show closer placement of molecules in crystal of **2** than that of **1**, an alternative way of showing these relations is the area of triangles (T1–T4, Table S3) delimited by crucial atoms. All triangles are smaller in **2** than in **1**. The D–H···A angles are between ca. 125 and 160°. The deviation from linearity (180°) is due to the bifurcated character of hydrogen bond bridges. It is also worth to stress that both hydrogen bond donors and acceptors are bifurcated. Moreover, the solved structures suggest that at times the interactions usually considered as weaker can support stronger ones and together with the ability of additional interactions by extra basic centers (N3) new, hardly predictable structures are formed [51]. To better understand the intermolecular interactions in these molecules computations were performed.

The QTAIM [52] is useful in describing the properties of hydrogen bond bridges, i.e., the electron density (ρ) and Laplacian of electron density ($\nabla^2\rho$) at Hydrogen Bond Critical Point (H-BCP). According to this method for the covalent bond the Laplacian of electron density at BCP is negative and for interactions of hydrogen bonding nature (H-BCP), it is positive [52, 53]. QTAIM data for currently studied interactions are collected in Table 2 (the geometry taken from XRD measurements).

It is worth to note that except for N7H7···N3' interaction (hydrogen bond distances, Table 1) the polarization of CH bond by chlorine atoms in **2** makes its hydrogen bonds stronger. Moreover, the hydrogen bond energies [54, 55] (E_{HB}) were calculated according to Espinosa approach [54, 55], while the overall interaction energy (E_{int}) is the difference between energy of the complex and the sum of energies of monomers. Espinosa's approach based on QTAIM and properties of hydrogen bond critical point

properties was used on a variety of non-covalent interactions including $XH\cdots O$ ($X = C, N, O$), $H\cdots F$ [54–59] hydrogen bonds. Moreover, the same approach has been used to study the hydrogen bond bridges in which the hydrogen bond acceptor carries three ($FH\cdots FF$ [58], $NH\cdots F$, $CH\cdots F$ [59]), two ($NH\cdots O$, or $OH\cdots O$ [54]), and one lone electron pair ($FH\cdots NH_3$ [59]). This method have also been used in explaining the properties of intramolecular hydrogen bonds ($NH\cdots N$ [60]) and intermolecular ones that stabilize dimer, trimers and tune the properties of rotamers in supramolecular assemblies [16, 61]. It is fair to mention that we used this approach to highlight the differences in energy of interactions between $NH\cdots N/O$ and $CH\cdots N/O$ contacts, while the QTAIM was shown to be applicable for many structures where the hydrogen bonding is described as purely non-covalent interaction (even a weak one [62]) or it is considered as partially covalent one with relatively high bond orders [63]. The same methodology may be applied to study hydrogen bonding in π -electron conjugated structures [64] or in investigations on halogen bonding [65]. E_{int} s are corrected to basis set superposition error (BSSE) with the counterpoise method [47, 66] as implemented in Gaussian [49] with default settings (see later in text).

To study the association of these molecules in solution the 1H NMR dilution experiments (in $CDCl_3$) were performed as before [9]. The dimerization constants (K_{dim}) at 293 K are 1.4 for **1** and $1.7 M^{-1}$ for **2**, respectively, when both NH and CH protons were used as probe nuclei [12].

It has been argued that generally the intramolecular hydrogen bonding is stronger than intermolecular [67]. In

addition, a weak $CH\cdots N$ interaction may have some influence on the conformational freedom in these compounds (Fig. 3).

The intramolecular hydrogen bond is a dominant interaction stabilizing the *closed* form in heterocyclic urea derivatives (Fig. 3). In **1** and **2** the *open* form is ca. 16 kJ/mol higher in energy than *closed* one. The energy of $CH\cdots N$ interaction, according to Espinosa [54, 55], is -12.8 kJ/mol in **1** and -17.4 kJ/mol in **2**. On the other hand, the *closed*–*open* form equilibrium may take place as the rotation about N7–C8 bond is easy and passes through the energetically low-lying transition state. The calculated barrier to rotation (transition state) about N7–C8 bond is ca. 59 kJ/mol with respect to the *closed* form.

In order to explain the intermolecular interactions in **1** and **2** and resulting solid-state structure the dimerization was considered as the initial step on way to higher aggregates. Therefore, the *open* and *closed* forms (Fig. 3) were optimized as dimers and the interaction energy together with QTAIM parameters were calculated. Figure 4 shows six dimers used in these calculations.

In Table 3 the results of calculations are collected, i.e., the interaction energy between molecules in kJ/mol corrected to BSSE (E_{int}), electron density at H-BCP (ρ), Laplacian of electron density ($\nabla^2\rho$), and energy of hydrogen bonds (E_{HB}). The geometry optimized in vacuum was used as initial geometry for calculations with the use of PCM [68] model of solvation and higher basis set (6–311+G(2d,2p), Table 3 in italics) for the associate that was found by X-ray crystallography (**D2**, Fig. 4). The same basis set was applied on the X-ray structural geometry as a single point runs (Table 2).

Fig. 4 Dimers **D1–D6** of **1** and **2**

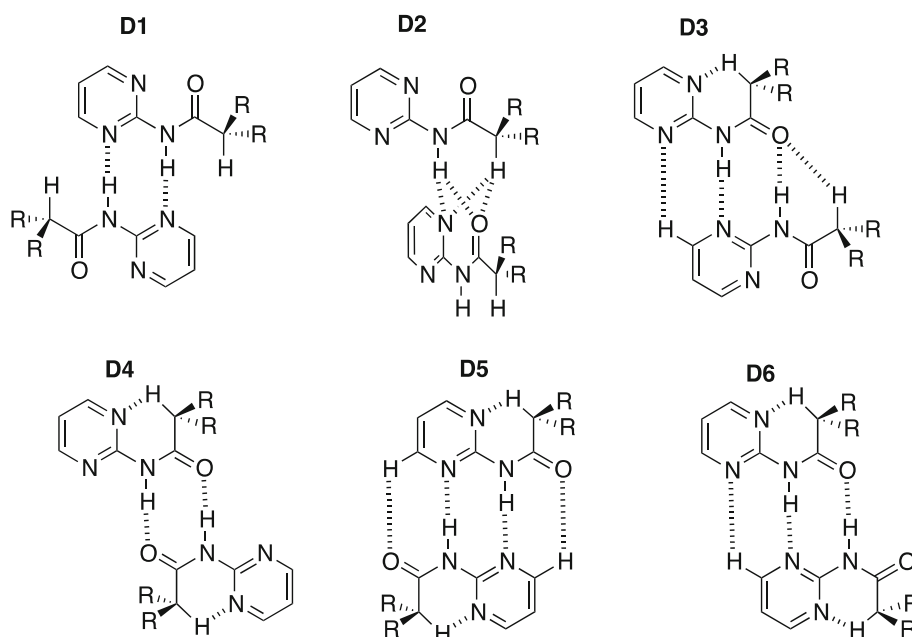


Table 3 Calculated properties of dimers at their H-BCP

	1 $E_{\text{int.}}, \rho, \nabla^2\rho, E_{\text{HB}}$	2 $E_{\text{int.}}, \rho, \nabla^2\rho, E_{\text{HB}}$
<i>Closed form</i> (CH...N)	–, 0.016, 0.055, –12.8	–, 0.021, 0.073, –17.4
D1 (NH...N)	–39.5, 0.023, 0.069, –18.3	–53.6, 0.025, 0.074, –20.6
D2 (NH...N)	–37.8, 0.009, 0.033, –7.3	–60.4, 0.017, 0.057, –13.2
(NH...O)	0.020, 0.08, –18.9	0.014, 0.053, –12.3
(CH...N)	H-BCP not found	H-BCP not found
(CH...O)	0.006, 0.017, –4.2	0.007, 0.027, –6.1
D2 (NH...N)	0.012, 0.041, –9.2	0.019, 0.064, –15.4
(NH...O)	0.017, 0.065, –14.8	0.011, 0.041, –9.5
(CH...N)	0.006, 0.017, –4.1	0.008, 0.026, –6.1
(CH...O)	0.007, 0.020, –5.1	0.013, 0.048, –10.8
D3 (NH...N)	–48.2, 0.026, 0.077, –22.1	–56.3, 0.028, 0.081, –24.2
(NH...O)	0.025, 0.095, –24.8	0.027, 0.099, –26.4
(CH...N) ^a	0.017, 0.060, –14.2	0.022, 0.078, –18.8
(CH...N) ^b	0.009, 0.026, –6.3	0.009, 0.025, –5.9
(CH...O) ^c	0.006, 0.023, –5.3	0.009, 0.033, –7.3
D4 (NH...O)	–31.8, 0.025, 0.095, –24.5	–36.6, 0.025, 0.094, –24.0
(CH...N)	0.017, 0.060, –14.1	0.023, 0.080, –19.6
D5 (NH...N)	–51.3, 0.026, 0.079, –22.6	–56.9, 0.027, 0.083, –24.5
(CH...N) ^a	0.017, 0.057, –13.4	0.022, 0.075, –17.7
(CH...O) ^b	0.010, 0.033, –8.1	0.010, 0.031, –7.5
D6 (NH...N)	–33.9, 0.026, 0.078, –22.0	–36.8, 0.027, 0.082, –24.2
(NH...O)	0.023, 0.087, –21.7	0.024, 0.089, –22.3
(CH...N) ^{a,d}	0.017, 0.059, –13.9	0.022, 0.077, –18.4
(CH...N)	0.017, 0.058, –13.6	0.022, 0.077, –18.5
(CH...N) ^b	0.010, 0.029, –6.9	0.009, 0.026, –6.3

^a Intramolecular hydrogen bond, ^b aromatic CH...N interaction, ^c –Cl₂CH...O hydrogen bond, ^d molecule that contains aromatic CH...N interacting proton (**D6**, bottom molecule, Chart 4)

In general the data for H-BCP calculated in vacuum, solvent, and from X-ray structure are in agreement. The CH...N/O interaction is stronger in **2** than in **1** due to the C–H bond polarization caused by the adjacent electronegative chlorines.

The data in Table 3 are in agreement with experimental findings. The dimer observed in 2-isobutyroylaminopyridine [9] and stabilized by NH...N hydrogen bond was not found in respective pyrimidine derivatives. The calculated data explain the stability of the 2-isobutyroylaminopyrimidine and respective dichloro derivative in crystal. The current data also show that the bifurcated character of hydrogen bonds is crucial in association of **1** and **2**. This is especially true for **2** where the weak interactions by CH group are strengthened by bond polarization. This conclusion is supported by the deshielding in ¹H NMR chemical shifts (ESI). The broadened ¹H signals of CH moieties in **1** and **2** suggest that this proton is interacting with nitrogen by weak hydrogen bonding.

Conclusions

The single crystal X-ray structures of two 2-acylamino-pyrimidines **1** and **2** reveal interesting NH...O/N and

CH...O/N interactions that have bifurcated character. The strength of intermolecular interaction depends on the presence of chlorines in the acyl moiety, which polarize the adjacent C–H bond. The quantum chemical calculations based on X-ray structures explain experimental findings. When compared with 2-acylamino-pyrimidines an extra nitrogen (N3) in the heterocyclic ring increases the number of energetically relevant dimeric structures. However, the crucial point is that the C–H bond polarization by chlorines in **2** results in the most stable structure being the dimer stabilized by bifurcated hydrogen bonds. Based on Jorgensen's approach the secondary interactions [69] rely mostly on the repulsive or attractive interactions in coplanar complexes. Dimers of **1** and **2** with bifurcated hydrogen bonds are nonplanar and do not favor the secondary interactions, especially strong repulsions. Moreover, the dimers with bifurcated hydrogen bonds are able to further aggregate in chain structures. Also, it is worth to mention that although the *closed* conformer of the monomer is the most stable form, the formation of intermolecular interactions can favor the *open* form in crystals due to relatively high rotational barrier between *open* and *closed* forms.

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References

- Prins LJ, Timmerman P, Reinhoudt DN (1998) *Pure Appl Chem* 70:1459
- De Greef TFA, Smulders MMJ, Wolffs M, Schenning APHJ, Sijbesma RP, Meijer EW (2009) *Chem Rev* 109:5687
- Prins LJ, Reinhoudt DN, Timmerman P (2001) *Angew Chem Int Ed* 40:2382
- Szyc Ł, Guo J, Yang M, Dreyer J, Tolstoy PM, Nibbering ETJ, Czarnik-Matusewicz B, Elsaesser T, Limbach H–H (2010) *J Phys Chem A* 114:7749
- Etter MC (1991) *J Phys Chem* 95:4601
- Aakeröy CB, Champness NR, Janiak C (2010) *Cryst Eng Commun* 12:22
- Sherrington DC, Taskinen KA (2001) *Chem Soc Rev* 30:83
- Steiner T (2002) *Angew Chem Int Ed* 41:48
- Ośmiałowski B, Kolehmainen E, Dobosz R, Gawinecki R, Kauppinen R, Valkonen A, Koivukorpi J, Rissanen K (2010) *J Phys Chem A* 114:10421
- Ośmiałowski B, Kolehmainen E, Gawinecki R, Dobosz R, Kauppinen R (2010) *J Phys Chem A* 114:12881
- Ośmiałowski B, Gawinecki R, Kolehmainen E, Kalenius E, Behera B, Kauppinen R, Sievanen E (2011) *Struct Chem* 22:1143
- Ośmiałowski B, Kolehmainen E, Kauppinen R, Kowalska M (2011) *Supramol Chem* 23:579
- Ośmiałowski B, Kolehmainen E, Gawinecki R, Kauppinen R, Koivukorpi J, Valkonen A (2010) *Struct Chem* 21:1061
- Gooch A, McGhee AM, Renton LC, Plante JP, Lindsay CI, Wilson AJ (2009) *Supramol Chem* 21:12
- Corbin PS, Zimmerman SC, Thiessen PA, Hawryluk NA, Murray TJ (2001) *J Am Chem Soc* 123:10475
- Ośmiałowski B, Kolehmainen E, Ikonen S, Valkonen A, Kwiatkowski A, Grell I, Haapaniemi E (2012) *J Org Chem* 77:9609
- Hunter C, Anderson H (2009) *Angew Chem Int Ed* 48:7488
- Manesiotis P, Hall AJ, Sellergren B (2005) *J Org Chem* 70:2729
- Jeoung E, Augier de Cremiers H, Deans R, Cooke G, Heath SL, Vanderstraeten PE, Rotello VM (2001) *Tetrahedron Lett* 42:7357
- Schmuck C, Wienand W (2001) *Angew Chem Int Ed* 40:4363
- Turi L, Dannenberg JJ (1993) *J Phys Chem* 97:7899
- Green RD (1974) *Hydrogen bonding by C–H groups*. Macmillan, London
- Desiraju GR (1991) *Acc Chem Res* 24:290
- Pierce AC, ter Haar E, Binch HM, Kay DP, Patel SR, Li P (2005) *J Med Chem* 48:1278
- Desiraju GR (1996) *Acc Chem Res* 29:441
- Xing L, Wiegert C, Petitjean A (2009) *J Org Chem* 74:9513
- Mambanda A, Jaganyi D, Munro OQ (2007) *Acta Crystallogr C* 63:0676
- Nishio M (2004) *CrystEngComm* 6:130
- Desiraju GR (2002) *Acc Chem Res* 35:565
- Dale SH, Elsegood MRJ, Hemmings M, Wilkinson AL (2004) *CrystEngComm* 6:207
- Singh D, Baruah JB (2009) *CrystEngComm* 11:2688
- Vishweshwar P, Nangia A, Lynch VM (2001) *J Org Chem* 67:556
- Bhogala BR, Nangia A (2003) *Cryst Growth Des* 3:547
- Hsu Y-F, Chen J-D (2004) *Eur J Inorg Chem* 2004:1488
- Nakagawa T, Immel S, Lichtenthaler FW, Lindner HJ (2000) *Carbohydr Res* 324:141
- Singha NC, Sathyanarayana DN (1997) *J Chem Soc Perkin Trans 2*:157
- Sudha LV, Sathyanarayana DN (1985) *J Mol Struct* 131:253
- Jiménez Blanco JL, Benito JM, Mellet CO, García Fernández JM (1999) *Org Lett* 1:1217
- Oertli AG, Meyer WR, Suter UW, Joho FB, Gramlich V, Petter W (1992) *Helv Chim Acta* 75:184
- Chantrapromma S, Fun H-K, Jana S, Hazra A, Goswami S (2008) *Acta Crystallogr E* 64:o267
- Wu X, Delgado G, Krishnamurthy R, Eschenmoser A (2002) *Org Lett* 4:1283
- Benesi H, Hildebrand J (1949) *J Am Chem Soc* 71:2703
- Zhao Y, Schultz NE, Truhlar DG (2005) *J Chem Phys* 123:161103
- Zhao Y, Truhlar DG (2006) *J Chem Theory Comput* 2:1009
- Zhao Y, Truhlar DG (2008) *J Chem Theory Comput* 4:1849
- Zhao Y, Truhlar DG (2008) *Theor Chem Acc* 120:215
- Peng C, Schlegel HB (1993) *Isr J Chem* 33:449
- Peng C, Ayala PY, Schlegel HB, Frisch MJ (1996) *J Comput Chem* 17:49
- Gaussian 09, Revision A.02, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J, J. A., Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) *Gaussian, Inc., Wallingford*
- Biegler-König F, Schönbohm J, Bayles D (2001) *J Comput Chem* 22:545
- Sureshan KM, Gonnade RG (2013) *CrystEngComm* 15:1676
- Bader RFW (1990) *Atoms in molecules: a quantum theory*. Oxford University Press, New York
- Popelier LA (2000) *Atoms in molecule. An introduction*. Pearson Education, London
- Espinosa E, Molins E, Lecomte C (1998) *Chem Phys Lett* 285:170
- Espinosa E, Souhassou M, Lachekar H, Lecomte C (1999) *Acta Crystallogr B* 55:563
- Espinosa E, Lecomte C, Molins E (1999) *Chem Phys Lett* 300:745
- Espinosa E, Molins E (2000) *J Chem Phys* 113:5686
- Espinosa E, Alkorta I, Rozas I, Elguero J, Molins E (2001) *Chem Phys Lett* 336:457
- Espinosa E, Alkorta I, Elguero J, Molins E (2002) *J Chem Phys* 117:5529
- Ośmiałowski B, Krygowski TM, Dominikowska J, Palusiak M (2011) *New J Chem* 35:1433

61. Ośmiałowski B, Kolehmainen E, Kowalska M (2012) *J Org Chem* 77:1653
62. Koch U, Popelier PLA (1995) *J Phys Chem* 99:9747
63. Grabowski SJ (2011) *Chem Rev* 111:2597
64. Sobczyk L, Grabowski SJ, Krygowski TM (2005) *Chem Rev* 105:3513
65. Grabowski SJ (2012) *J Phys Chem A* 116:1838
66. Boys SF, Bernardi F (1970) *Mol Phys* 19:553
67. Etter MC (1990) *Acc Chem Res* 23:120
68. Tomasi J, Mennucci B, Cammi R (2005) *Chem Rev* 105:2999
69. Jorgensen WL, Pranata J (1990) *J Am Chem Soc* 112:2008
70. Farrugia L (1997) *J Appl Crystallogr* 30:565